

using a cone-plate viscometer at a uniform Brookfield LDV III shear rate;

- 5 - they were measured in 0.5 M aqueous LiNO_3 solution at 20°C using 4 Shodex OH Pack B803 to B806 columns of 25 cm in series, with refractometric detection. They are expressed in 10^6 g/mole. The values in brackets are the values in "POE equivalent" (obtained by comparing with polyoxyethylene standards), with refractometric detection.

15 The copolymer T10 as well as other copolymers of the same family not described here were also analyzed in terms of molecular mass using multiangle laser light scattering detection ("MiniDawn Wyatt"), which makes it possible to obtain the absolute molecular mass. By comparing with the masses, as "POE equivalent", of the same polymers, it was evaluated that, for all the

20 polymers presented in Table 2, the absolute molecular mass is of the order of twice the mass as POE equivalent: this estimated value is given in bold characters in the table.

25 Knowing the average molecular mass of the copolymers, that of the segments with LCST or macromonomers, and the fraction by mass of segments with LCST incorporated into the copolymer, the average number of segments with LCST per polymer (average values by mass), noted N_s in

30 Table 2, can be easily deduced by means of the formula:

$$N_s = f M_w(\text{copolymer}) / M_w(\text{macromonomer})$$

35 - The values in bold represent the fraction f of segments with LCST in the final copolymer (fraction by mass).

All the copolymers described in Table 2 exhibit a thermoviscosifying character.

TABLE 2

Co-polymer	Monomer	Macromonomer	Na ₂ S ₂ O ₅	Preparation temperature	Viscosity at 25°C	Viscosity at 60°C	Mw	Mw/Mn	Ns
T7	DMAM (2.8 g)	PNIPAM-10 (0.7 g)	5 g/l	29°C	500	8000	ND	ND	ND
T10	AM (2.8 g)	PNIPAM-10 (0.4 g)	5 g/l	29°C	1000	11000	(1.48) 3	4	10
T10AA	AM (2.8 g)	(0) 0	5 g/l	29°C	800	700	(0.93) 2	2.4	0
T11	AM (2.8 g)	PNIPAM-10 (0.8 g)	20 g/l	23°C	100	1000	(0.38) 0.75	3.6	4
T12	AM (2.8 g)	PNIPAM-5 (0.8 g)	20 g/l	23°C	30	2000	(0.37) 0.75	4.8	7
T13	AM (2.8 g)	PNIPAM-5 (0.8 g)	10 g/l	23°C	100	10000	ND	ND	ND
T15	AM (2.8 g)	PNIPAM-5 (0.4 g)	5 g/l	25°C	200	13000	ND	ND	ND
T16	AM (2.8 g)	PNIPAM-5 (0.4 g)	5 g/l	29°C	800	15000	(1.1) 2.2	2.2	11
T21	AM (2.8 g)	PNIPAM-20 (0.8 g)	20 g/l	23°C	30	1800	ND	ND	ND
T22	AM (2.8 g)	PNIPAM-20 (0.4 g)	5 g/l	23°C	ND	ND	(1.0) 2	5	4
T24	AM (2.8 g)	PNIPAM-M (0.4 g)	5 g/l	29°C	ND	ND	(1.4) 3	6.6	12
T25	AM (2.8 g)	PNIPAM-C (0.4 g)	5 g/l	29°C	ND	ND	(1.1) 2.2	4.9	13
T26	AM (2.8 g)	PNIPAM-L (0.4 g)	5 g/l	24°C	ND	ND	(1.5) 3	4.7	8

The procedure presented below is given for the preparation of the copolymer T7. The procedures for the other copolymers may be deduced therefrom by modifying the nature and the concentration of the reagents, and optionally the reaction temperature in accordance with Table 2.

PNIPAM-10 and the monomer considered as well as 30 ml of distilled water are introduced into a 100 ml round-bottomed flask. This mixture is stirred for two hours at room temperature with bubbling of nitrogen so as to remove the dissolved dioxygen.

The mixture is then heated to the temperature chosen for the polymerization using a thermostated bath and the initiators are then added in the form of a solution of $(\text{NH}_4)_2\text{SO}_8$ at 20 g/l and a solution of $\text{Na}_2\text{S}_2\text{O}_5$ at 5 g/l, that is 0.1% and 0.03% by mole, respectively, of the quantity of monomers introduced. The stirring and the bubbling are maintained for 4 hours.

Before introducing the initiators, and then every hour during the polymerization, samples of the reaction medium are collected (0.1 ml diluted in 5 ml of methanol) in order to monitor the variation of the reaction by steric exclusion chromatography.

Generally, the data associated with the visual observation of the increase in the viscosity of the reaction medium make it possible to conclude the good progress of the reaction, with a practically total yield.

b) Purification

The purification of the polymers is carried out differently depending on the nature of the skeleton.